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Part I

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Polymerization Kinetics by Means of Differential Thermal Analysis

Part I. Apparatus

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Part I

FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Laboratory. This work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Dr. W. E. Gibbs acting as project engineer.

This report covers work accomplished from October 1961 to October 1962.

ABSTRACT

A differential thermal analysis (DTA) apparatus has been designed to determine kinetic and thermodynamic data from polymerization reactions. The apparatus was calibrated and the decomposition rate of azobisisobutyronitrile was determined. The data obtained are in good agreement with those reported in the literature.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

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INTRODUCTION

The development of differential thermal analysis can be traced back over 75 years to LeChatelier who first applied it in an investigation of the constitution of clays (ref 1). The principle of this method consists in placing the substance under investigation together with an equal amount of an inert material in a furnace. The furnace temperature is then raised at a constant rate and the difference in temperature between the two juxtaposed materials is recorded. This is usually accomplished by means of a differential thermocouple. By placing one junction into the material to be investigated and the other into the inert reference substance, the e.m.f.'s developed in the two junctions are continuously compared. The differential e.m.f., being proportional to the differential temperature, is amplified and plotted. Thermal changes in the sample show up as deviations from the otherwise straight baseline.

Until recently, differential thermal analysis has been primarily used in mineralogy, soil studies, and with inorganic materials. In recent years, it has been increasingly applied to organic problems and, most notably, in evaluating the thermal stability of organic materials.

During World War II, Spiel (ref 2) derived equations showing that under certain conditions the area under the DTA curve is proportional to the heat of reaction. The conditions under which this holds true are that the cells containing the materials have the same shape, that there are no thermal gradients within the sample and within the furnace, and that the thermal conductivity and heat capacity of active and inert materials are alike. When these conditions are satisfied:

$$\Delta H = KA, \quad (1)$$

where K is a constant, characteristic of the apparatus used and of the conditions described above. Spiel's equation was experimentally verified by several workers in the field (refs 4 and 5). As a consequence a variety of apparatus was designed in order to use this means of measuring heat of reaction, one example being the aluminum block system developed by Borchardt (ref 3). The same author together with F. Daniels extended this technique to encompass the field of solution reactions (ref 6). It was found that DTA of solutions tends to meet the postulated conditions much better than is the case with solids. The thermal gradients within the sample as well as the ambient temperature can now be controlled by adequate stirring. In dilute solution the heat capacities of the reference cell (containing pure solvent) and the sample cell (containing solution) will tend to be nearly identical and, inasmuch as the cells are identical in size and shape, the volumes and therefore the heat capacity per unit volume will also tend to be the same. Borchardt and Daniels extended Spiel's formula into solution reactions by assuming that the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time:

$$dH/dt = dn/dt; dH = - \frac{KA}{n_0} dn \quad (2)$$

In further developing this assumption they arrived at an equation, giving the actual rate of reaction at any temperature in terms of the slope and height at that temperature (figure 1):

$$-\frac{dn}{dt} = \frac{n_0}{KA} \left[C_p \frac{d\Delta T}{dt} + K \Delta T \right] \quad (3)$$

The number of moles present (n) at any instant is equal to the initial moles (n_0) minus the number of moles that have reacted. Substituting in equation (4), integrating, and rearranging gives

$$k = \frac{C_p \frac{d\Delta T}{dt} + K \Delta T}{[K(A-a) - C_p \Delta T]^x} \quad (4)$$

where k = rate constant of a reaction of order x , $A-a$ is the remaining area under the curve (figure 1), and $d\Delta T/dt$ is the slope of the curve at the temperature at which k is being evaluated.

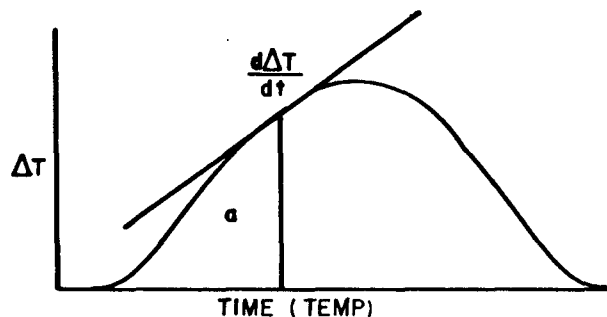


Figure 1. DTA Curve

The authors show further that very little error results from eliminating the heat capacities from the equation, since the heat capacity of solvent and reactant tends to be the same provided the solution is dilute. The order of magnitude of this term is, moreover, so small in comparison to the other terms that it can safely be neglected. This simplifies equation (4) to

$$k = \frac{\Delta T}{A-a} \quad (5)$$

The important terms are therefore the height (ΔT) and the remaining area under the curve ($A - a$), both of which can be measured accurately. From these data the activation energy can then be determined. It should be pointed out that this plot will result in a straight line only when the correct value for x has been assumed. From equation (1) the heat of reaction can be calculated. In addition to heat of reaction and reaction rates, it is thus possible also to obtain the frequency factor and the activation energy by substitution into the Arrhenius equation.

Part I

Although the above work dealt primarily with reactions involving relatively small molecules, there was reason to believe that with suitable modification it would also be possible to extend this approach to a study of polymerization reactions. The total heat of reaction in a polymerization can be expressed by

$$\Delta H = \sum (\Delta H_i + \Delta H_p + \Delta H_t + \Delta H_{ct} + \dots) \quad (6)$$

where i = initiation, p = propagation, t = termination, ct = chain transfer. The relative order of magnitude of these terms is such that the bulk of the reaction takes place in the steady state so that a relatively small error is introduced by ignoring the other terms. The present lack of heat data for polymerization reactions stems from the fact that it requires tedious and time consuming calorimetric techniques. The successful application of DTA to this area would therefore fill a definite need not only for enthalpy but rate data as well and would result in a reduction in time necessary for such determinations from months to a matter of hours.

EXPERIMENTAL

A. Apparatus

The original set-up resembled that used by Borchardt and Daniels (ref 6) but proved to be unsuitable for polymerization reactions. The equipment was therefore extensively modified and redesigned as follows:

1. The bath size was increased to a capacity of approximately 10 gallons (12 in. ID., 22 in. deep).
2. The cell size was increased to 350 cc capacity (2 Pyrex tubes 8 in. long, 2 in. wide) and the thermocouples were encased in glass tubes and rigidly positioned by means of a standard taper joint in the cell wall; vane-type stirrer blades were selected with a view toward uniformity of the blade.
3. The supporting structure was redesigned to permit reproducible repositioning of the cells. Micrometer heads were installed to facilitate small changes in the vertical position of the cells.
4. The wall wire heaters were discarded in favor of 3 concentric strip heaters attached to the exterior of the bath bottom. The total capacity of these heaters was 4000 watts, permitting heating rates from 0.6° to 2.3°C/min.
5. The multiple bath stirrer system was replaced by a single $\frac{1}{2}$ hp. induction motor which, in contrast to the previous set-up, did not interfere electrically with the sensitive recording equipment.
6. The latter consisted of a recorder (scale -1 to 10 mv.), a d.c. amplifier (range: 100 mv. to 0.1 μ v. at full scale), and an integrator-counter which automatically counts the area under the curve and provides a digital readout.
7. Stirring of the test cells was maintained by two separate, speed-controlled stirrers. With the previously used single stirrer-pulley arrangement uneven stirring rates were obtained because of friction in the stirrer bushings. Several types of lubricants were unsuccessfully tried before the set-up was finally changed to a direct-drive mercury seal design.

8. It was further found that the stirring rate in the two cells must be identical if baseline deviations were to be avoided. This was accomplished by means of a stroboscope.
9. The bath temperature was recorded separately on the chart by means of an iron-constantan thermocouple.
10. Lubricating oil, Spec. MIL-L-7808, having the proper viscosity-temperature characteristics, was selected as bath fluid.

In all experiments lamp-grade nitrogen was bubbled through the solvent prior to each run and a blanket of nitrogen was kept over the fluid throughout each run. Diethyl- or dibutyl phthalate were used as solvents.

Several experiments were carried out in order to study baseline drift and its contributing factors. It was found that an important source of drift is the location of the test cells, both relative to each other, as well as to their placement in the bath, so that a position had to be found where the temperature difference between cells remained constant throughout the temperature range. This proved to be more important than reducing the initial temperature difference between cells to a minimum.

B. Calibration

The differential thermocouple (copper-constantan) was calibrated, using two Beckman thermometers in two one-liter Dewar flasks. The e.m.f. found, 39.08 microvolts/°C at 13.80°C was identical with the literature value. The pen displacement was found to be 13.03 inches per °C, or 0.7676°C for a full scale deflection (10 inches) at a range of 30 μ v.

In order to eliminate the effect of temperature difference between that of the cell contents and that of the test solution to be added, the latter was stored in a jacketed microburette. An eight-inch hypodermic needle extended from the burette into the cell. Water was pumped from a constant temperature bath maintained at a slightly higher temperature through the jacket surrounding the microburette. It was found that if the constant temperature water bath was maintained about 10°C above that of the oil bath, no baseline deviations were noted when adding water to water in the cell.

A series of screening experiments were run and zinc chloride was selected as a suitable calibration test material. (Pure zinc chloride hydrate was prepared by reacting 99.9 percent pure zinc metal with conc. HCl, followed by washing, filtering, and drying at 110° overnight.) One hundred grams of distilled water was added to each cell; the cell stirrer speed was adjusted to 1500 rpm; from the microburette an accurate quantity (3-4 ml.) of zinc chloride in water was added to one cell and the evolved heat was recorded. Preliminary experiments had shown that the pH of the solution had to be kept on the acid side by prior addition of 2-3 drops of 9N HCl in order to prevent side reactions, such as the formation of $\text{Zn}(\text{OH})_2$, the precipitation of which tended to obscure the results. The calibration data are given in table 1.

TABLE 1
CALIBRATION OF TEST CELL

	1	2	3	4
ZnCl ₂ added (moles x 10 ²)	0.9164	0.9622	0.8840	1.0404
Molar Ratio H ₂ O/ZnCl ₂	613.4876	606.2679	656.2738	566.2520
Δ H _{dil} (cal) (7)	46.33	48.61	44.88	52.35
Area (sq in.)	8.40	8.80	8.50	8.90
K (cal / ln. ²)	5.52	5.52	5.28	5.83

C. Determination of Initiator Decomposition Rates

The thermal decomposition of azobisisobutyronitrile (AIBN) has been studied by Arnett (ref 8) and Bawn (ref 9) who report the following rate constants, respectively:

$$k = 1.07 \times 10^{16} \exp \left\{ -32.1 \text{ kcal} / RT \right\}$$

$$k = 1.0 \times 10^{15} \exp \left\{ -30.7 \text{ kcal} / RT \right\}$$

Two determinations were carried out, using 100 g of di-n-butylphthalate as the solvent and 1.1677 g (0.0071 moles) and 0.9700 g (0.0059 moles) of AIBN, respectively. The cells were flushed with nitrogen for 30 minutes and were kept under a slight positive nitrogen pressure throughout the run. The heating rate was 1.83°C/min. The reaction started at 75-78°C, the peak was reached at 110°C, and it ended at 132-135°C. The data are given in table 2. A typical DTA decomposition curve of AIBN is shown in figure 2, and the activation energy plot is shown in figure 3.

TABLE 2
FIRST ORDER RATE CONSTANTS FOR THE THERMAL DECOMPOSITION OF AIBN

1. 0.0071 moles AIBN		2. 0.0059 moles AIBN	
T (°C)	k (sec ⁻¹)	T (°C)	k (sec ⁻¹)
85.8	1.33 x 10 ⁻⁴	92.0	3.00 x 10 ⁻⁴
93.9	3.47 x 10 ⁻⁴	98.0	7.58 x 10 ⁻⁴
100.7	8.57 x 10 ⁻⁴	105.0	1.56 x 10 ⁻³
107.9	1.95 x 10 ⁻³	110.8	3.03 x 10 ⁻³
114.5	4.28 x 10 ⁻³	117.0	5.92 x 10 ⁻³
119.8	6.48 x 10 ⁻³	120.5	8.02 x 10 ⁻³
125.0	9.72 x 10 ⁻³	124.0	8.97 x 10 ⁻³

The area under the curves was 48.38 and 36.16 sq in, respectively.

The heat of reaction, ΔH , was found to be -37,500 kcal/mole and -34,000 cal/mole, the activation energy 32.1 kcal. and 31.6 kcal., and the frequency factors 4.8×10^{15} and 2.8×10^{15} , respectively. These values are in good agreement with those reported in the literature (refs 8 and 9).

These preliminary experiments served to demonstrate the reliability of the apparatus. The next phase of this work will deal with kinetic and thermodynamic studies of polymerization reactions.

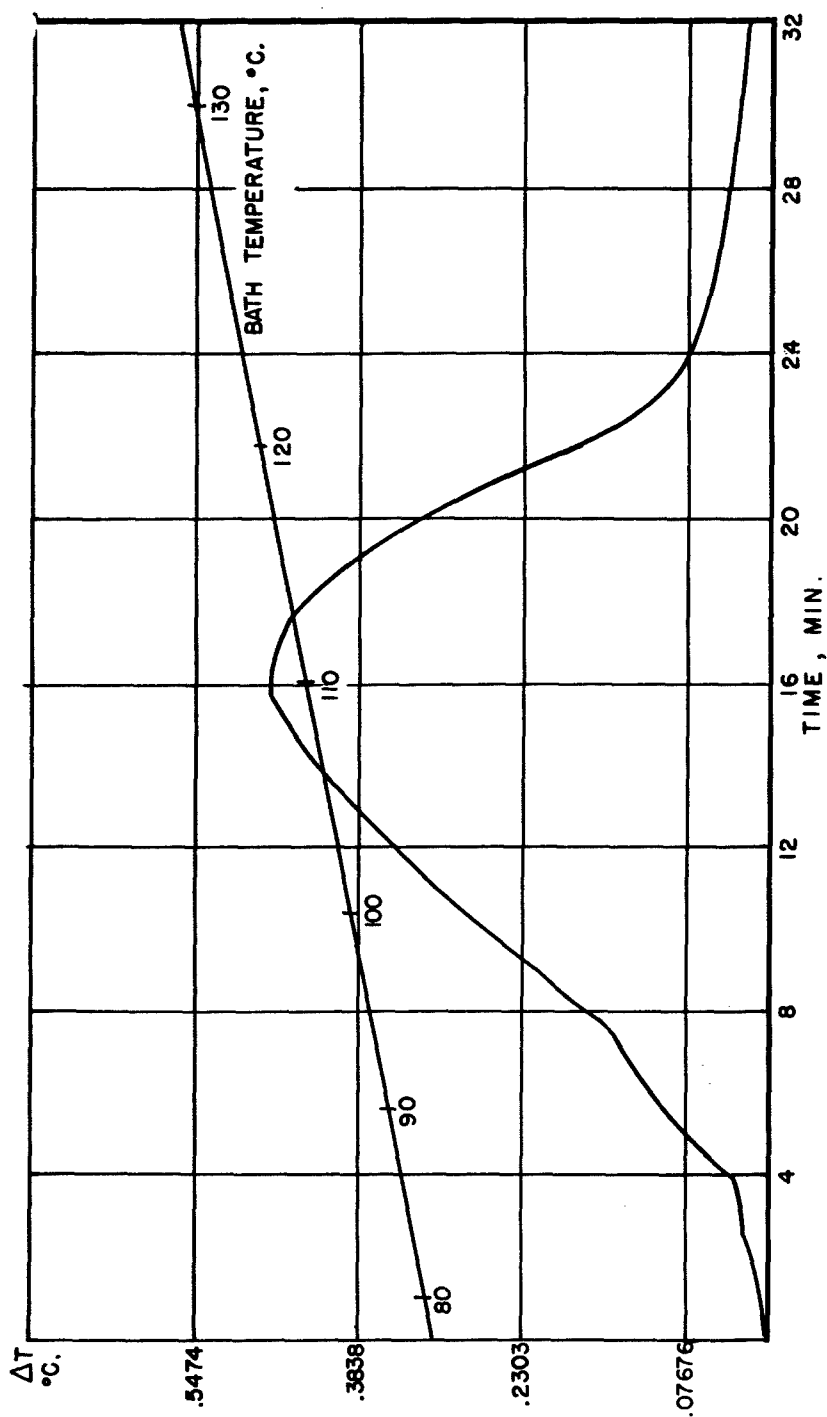


Figure 2. DTA Curve of AIBN Thermal Decomposition

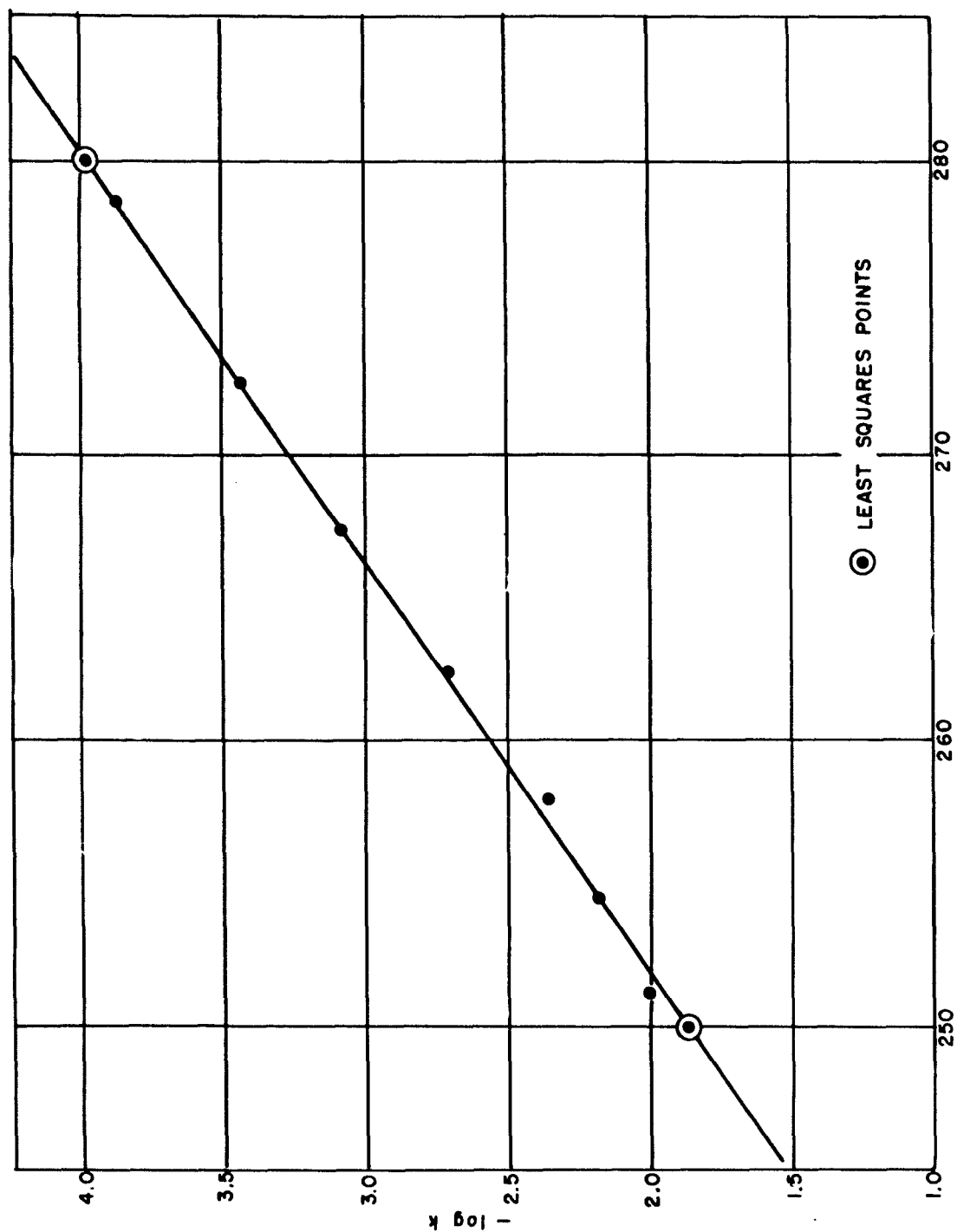


Figure 3. First Order Activation Energy Plot for the Thermal Decomposition of AIBN

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2. Differential thermal analysis
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